Simulation of microdisc problem in spherical co-ordinates. Application to electrogenerated chemiluminescence

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There are many analytical approximations and digital approaches for solution of microdisc problem. We demonstrate a new approach for digital solution of 2D microdisc problem in spherical co-ordinates and application it to solution of the non-steady state electrochemiluminescence (ECL) problem at a microdisc electrode.

ECL of electrolyte solutions results from the electron transfer (ET) reactions of electrogenerated ion radicals of an organic depolarizer that is capable of luminescence at the macro electrodes, and at a microelectrode. The ECL intensity is a quantitative characteristic of the rate of such ET reactions, and it provides information not only about the nature of exothermic ET reactions, but also about the properties of the electrode-solution interface, which is close to where these processes occur. ECL quantum contains information both on the kinetics of the heterogeneous electrode processes and on the subsequent homogeneous chemical reactions in the solution. Therefore, ECL can be used to analysis of solutions (for example, as a label in immunoassays) and to image electrode surfaces.

Our approach bases on idea to solve this problem instead of cylindrical (R, Z) in spherical co-ordinates (R, Θ)[1]. We have a large sphere (with radius equal cm) as insulator and microdisc electrode (radius equal microns) on the surface sphere. When $r_d << r_{sph}$ we assume that microdisc electrode surface is almost plane. This fact allows to compare calculated results with traditional solutions in cylindrical co-ordinates [2-5].

ECL involves the formation of electronically excited states by an energetic ET between redox species generated at an electrode surface. In this work the mass transport diffusion-controlled kinetics in an ECL cell with a microdisc electrode on large spherical insulator (Fig. 1) under bipolar impulse non-steady electrolysis is considered. Microdisc in an ECL cell is electrolysed by bipolar voltage impulses of amplitude being enough to form reduced and oxidised organoluminophor forms.

Simulation area is (Fig. 1)

$$r_{sph} \le r \le r_{max} = r_{sph} + 6\sqrt{D\,T_e}\,;$$

$$0 \le \Theta \le \Theta_{max} = \frac{r_d + 6\sqrt{D\,T_e}}{r_{sph}},$$

where T_e is the total electrolysis time, *D* is the diffusion coefficient, which is considered equal for every kind of species in the solution, r_d is the disk radius, r_{sph} is the sphere radius.

We used this idea for solution of microdisc problem and applied to ECL during non-steady state bipolar impulse electrolysis, and compared our new results with previous solutions for microdisc problem [6].

This approach gives a best convergence then like simulation of microdisc problem in cylindrical co-ordinates.

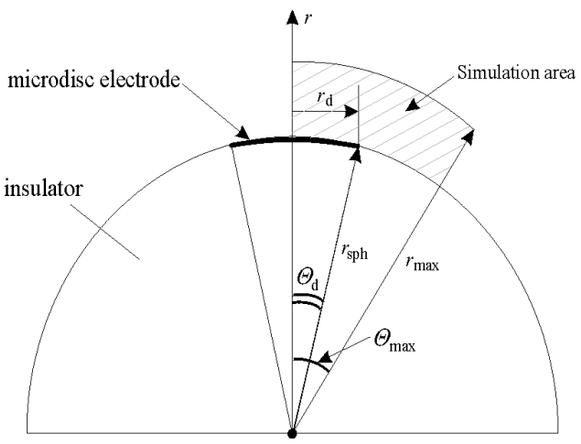

Fig. 1 Sheme of microdisc surface on the large sphere.

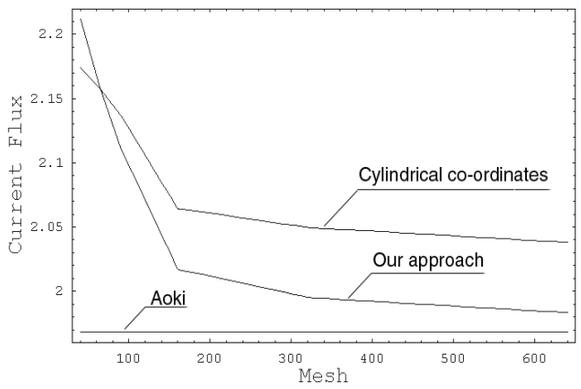

Fig. 2. A comparison of current flux for time point t = 7.84e-3

Fig. 3 The mean values of ECL intensity for two different approaches: Amatore transformation and this work.

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